CHARACTERIZATION AND PRODUCT IDENTIFICATION OF SLUDGE OBTAINED FROM THE RECYCLING OF LUBRICANT INTO BASE OIL

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ABSTRACT

This study describes the characterization and product identification of sludge that is obtained from the recycling of spent lubricant into base oil. Sludge is produced from the recuperation of spent lubricant which involves two main processes. The first process is to produce the solvent that will be used. The solvent consists of Hexane, Isopropanol (IPA) and Potassium hydroxide (KOH). The next process is the recuperation of used lubricant using the solvent produced. The ratio of spent lubricant and solvent used is 1:4. Physical mixing is then used to produce a natural reaction between the solvent and spent lubricant. The mixture is stirred continuously for 30 minutes. The stirred mixture is then filtered. There are two ways to filter the mixture. One is by centrifugation and the other is filtration with thin filter papers. The residue that is left behind is the sludge that is going to be used for the characterization process. Many parameters of the sludge is investigated and characterized before product identification is done. Both physical and chemical parameters are investigated. The parameters investigated are pH, density, viscosity, heavy metal content and chemical composition of the sludge. The pH of sludge on average is 6.59 with an average density of 0.9041 g/ml or 904.13 kg/m^3. The average viscosity is 1419 cP. There is a fair amount of heavy metals present in the sludge and its chemical composition consists of paraffin and olefins. From the results obtained, the sludge can be singled out for its major components and the contents can be derived into useful products. Three different products are identified. The sludge can be used as raw material for pyrolysis where the end product obtained is a diesel like liquid and also as concrete or cement additive. The sludge can also be used as grease.

ABSTRAK

Kajian yang dijalankan adalah tentang analisis dan pengenalpastian produk daripada sisa mendapan minyak yang terhasil daripada proses kitar semula minyak pelincir yang telah digunakan. Minyak pelincir yang telah digunakan dikitar semula menjadi minyak asas untuk penghasilan minyak pelincir. Sisa mendapan minyak yang dihasilkan melibatkan dua proses iaitu proses penyediaan pelarut dan seterusnya proses memisahkan sisa mendapan minyak dari pelarut. Pelarut yang digunakan dihasilkan dengan mencampurkan Heksana, Isopropanol (IPA) dan Kalium hidroksida (KOH). Pelarut yang terhasil ditambah kepada minyak pelincir terpakai dengan nisbah 4 bahagian pelarut kepada 1 bahagian minyak pelincir. Terdapat 2 cara untuk mengasingkan larutan minyak asas daripada sisa mendapan minyak yang terhasil. Proses pengasingan ialah dengan proses sentrifugasi dan juga dengan penapisan menggunakan kertas turas yang nipis. Sisa yang tertinggal ialah sisa mendapan minyak yang akan dianalisis. Parameter yang dikaji ialah dari segi fizikal dan kimia sisa mendapan minyak yang terhasil. Parameter yang dikaji ialah pH, kelikatan, ketumpatan, kandungan logam berat dan juga komposisi kimia sisa mendapan minyak. pH sisa mendapan minyak ialah 6.59 dengan ketumpatan sebanyak 0.9041 g/ml atau 904.13 kg/m^3. Kelikatan sisa mendapan minyak ialah 1419 cP. Sisa mendapan miyak yang terhasil mengandungi sisa logam berat dan komposisi kimia yang dikenalpasti ialah ia terdiri daripada parafin dan olefin. Dari keputusan kajian yang dibuat,produk daripada sisa mendapan minyak boleh dikenal pasti. Tiga produk yang boleh terhasil daripada sisa mendapan minyak. Sisa mendapan minyak boleh digunakan sebagai bahan mentah untuk proses pirolisis untuk penghasilan cecair seperti diesel dan juga sebagai penambah untuk simen dan konkrit. Sisa mendapan minyak juga boleh digunakan sebagai gris.

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LIST OF ABBREVIATIONS

KOH - Sodium Hydroxide

IPA - Isopropanol

RPM - Revolution Per Minute

HC - Hydrocarbon

AAS - Atomic Absorption Spectrometer

FAAS - Flame Atomic Absorption Spectrometer

IR - Infrared

FTIR - Fourier Transform Infrared

cP - Centi Poise

ppm - Particles Per Million

µm - Micrometer

MSDS - Material Safety Data Sheet

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CHAPTER 1

INTRODUCTION

1.1 Research Background

A lubricant is a substance introduced between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective film which allows for two touching surfaces to be separated and "smoothed," thus lessening the friction between them. The lubricant must be replaced when it has dissolved to its saturation point, because the inability to dissolve additional abrasive debris allows abrasive particles to scrape against or become lodged in the working surfaces, thus introducing a margin for physical contact between them.

One of the single largest applications for lubricants, in the form of motor oil, is to protect the internal combustion engines in motor vehicles and powered equipment (Boughton and Horvath, 2003). Typically lubricants contain 90% base oil and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefin, esters, silicone, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation (El-Fadel and Khoury R. M., 2004).

Base oil is nowadays produced by recycling spent lubricants. The recycling of lubricants to get base oil produces sludge as a by-product. Sludge is the residual semi-solid material left from industrial treatment processes (Norris S. and McCalmont M., 2005).

Oil sludge or black sludge is a solid or gel in motor oil caused by the oil gelling or solidifying. Sludge can be a major contributor to engine problems, and can require the engine to be replaced if the damage is severe. Sludge is usually caused by the presence of water in the oil, and can accumulate with use. Ways to minimize sludge production and accumulation include performing frequent oil changes, using synthetic oil, and following the manufacturer's engine maintenance routine (Synthetic Performance Solutions, 2007-2008).

Base oil and sludge separation covers a broad spectrum of separation processes. There are many ways employed for the separation depending on the situation. The base oil and sludge exist as an emulsion naturally. The base oil and sludge also contains the solvent that is used for the recycling process. Therefore further separation like evaporator is needed to produce base oil and sludge. If allowed to stand the emulsion will separate because base oil is lighter than the oil sludge. This process however is very slow and needs a lot of time for the separation to occur. The separation will also not be complete by natural gravitation force.

There are several ways for separation of sludge such as centrifuge and also through traditional method of filtration using thin filter paper. Thin filter paper is used as the oil sludge is in its semi solid state and it is easily separated.

1.2 Problem statement

It is estimated that 40 percent of all lubricants are released into the environment regarding its state whether it is in solid, semi-solid or liquid state. One of the lubricant wastes that are disposed is the sludge which is formed from the long usage of lubricants and also as a by-product from the recycling process. This sludge cannot be reused and this makes it to be disposed. The sludge contains a fair amount of oil and also heavy metals in it.

With today's knowledge, understanding and laws it is clear that to prevent soil and water contamination, we must properly dispose of oil wastes. Lubricants both fresh and used can cause considerable damage to the environment, mainly due to their high potential of serious water pollution. Further, the additives typically contained in lubricant can be toxic to flora and fauna.

There are ways to dispose used lubricants but it is not a safe way as it possesses its own hazards after the used lubricants are treated. Recycling, burning, landfill and discharge into water may achieve disposal of used lubricant. There are typically strict regulations in most countries regarding disposal in landfill and discharge into water as even a small amount of lubricant can contaminate a large amount of water. The lubricant can also be burned as fuel to generate electricity. Burning generates both airborne pollutants and ash rich in toxic materials, mainly heavy metal compounds.

Unfortunately, most lubricant that ends up directly in the environment is due to general public discharging it onto the ground, into drains and directly into landfills as trash. Other direct contamination sources include runoff from roadways, accidental spillages, natural or manmade disasters and pipeline leakages.

Improvement in filtration technologies and processes has now made recycling a viable option now with the rising price of base stock and crude oil. This recycling process produces sludge as a by-product. Typically various filtration systems remove particulates, additives and oxidation products and recover the base oil. The oil may get refined during the process. This base oil is then treated much the same as virgin base oil. However there is considerable reluctance to use recycled oils as they are generally considered inferior. The cause for this consideration by the public is because the lack of public awareness towards the usage of recycled base oil. More and more public awareness programs should be carried out to educate the people about the advantage of recycling. This will create more user friendly recyclers among the public thus recycling will be a viable option and there will be an increase in the usage of recycled base oil.

1.3 Objective

1. To obtain oil sludge in a lab scale.
2. To determine the suitable sludge filtration method in order to obtain large quantity of sludge.
3. To analyze the contents of oil sludge from the recycling process of lubricant into base oil
4. To identify the uses of oil sludge as a useful product.

1.4 Scope of Research

The scope of this experiment is to obtain oil sludge and to analyse the contents of it from the recycling process of lubricant into base oil. To achieve the objectives of this experiment, the following aspects have been identified:

i. Production of oil sludge by performing small scale base oil recuperation from used lubricant
ii. Determination of oil sludge characteristic using pH meter, Viscometer, Atomic Absorption Spectrometer (AAS) and Fourier Transform Infrared (FTIR).
iii. To identify the uses of oil sludge as a useful product.

1.5 Rationale and significance

Used oil is one of the most common wastes produced. In fact, approximately 4 billion gallons are generated every year worldwide. Used oil is generated by vehicle maintenance and repair facilities as well as various industrial areas. It is illegal to dispose of used oil in sewers, storm drains, waterways, on the ground or in the trash. Used oil can contain harmful contaminants that can work their way into our ground and surface waters and cause serious pollution. Just one gallon of used oil can contaminate a million gallons of drinking water. To cope with the polluting

factor, used lubricant oil is recycled into base oil. The process produces oil sludge as a by-product and this creates another problem as the sludge contains a fair amount of oil and also heavy metals in it. The use of base oil from the recycled lubricant is also far cheaper if compared to the virgin base oil that is produced. Therefore it is a better way to recycle used lubricant and find a useful product for the sludge that is obtained as a by-product.

CHAPTER 2

LITERATURE REVIEW

It is estimated that less than 45% of used engine oil is being collected worldwide while the remaining 55% is thrown by the end user in the environment (Boughton and Horvath, 2003).

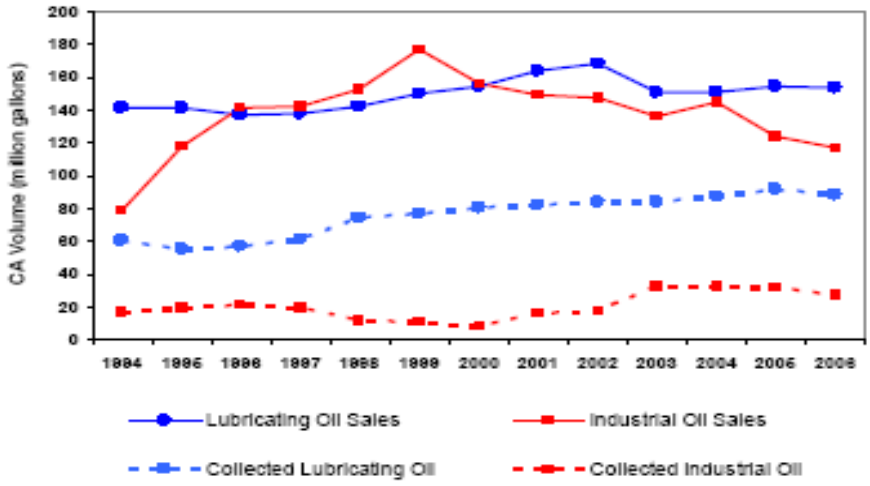

Figure 2.1: Oil sales and used oil collection trends, 1994-2006 (Tocci and Lisa, 2008).

Oil sludge or black sludge is a solid or gel in motor oil caused by the oil gelling or solidifying, usually at temperatures lower than 100^0C. Sludge can be a major contributor to internal combustion engine problems, and can require the engine to be replaced, if the damage is severe. Sludge is usually caused by the presence of water in the oil, and can accumulate with use. Ways to minimize sludge production and accumulation includes performing frequent oil changes, using synthetic oil and

following the manufacturer's engine maintenance routine (Norris S. and McCalmont M., 2005).

Sludge formation begins when suspended particles and other contaminants begin to settle out of the oil. Most oils contain additives to manage the contaminants, but if the oil is not changed often enough the additives will become overwhelmed. This happens when there are too many contaminants to handle or when the oils chemical properties are weakened from over use. Additives deplete over time from oxidation and heat resulting in changes to the chemical makeup of the oil itself (Kaufman M., 2002).

This sludge then begins to deposit on engine parts, obstructing the flow of oil and the proper transfer of heat away from metal parts. Oil sludge will begin to blanket the surfaces of the engine and clog oil channels eventually resulting in oil starvation to parts of the engine. When an engine runs, it takes in air from its current environment, mixes it with fuel and ignites it. The air and fuel mixture undergoes a chemical reaction and several by-products are produced. These by-products make their way into the engine oil through cylinder blow-by and exhaust gas recirculation and further contaminating the oil (Kaufman M., 2002).

Engine oils often contain detergents and dispersants as part of their additive packages which suspend and in some cases neutralize these contaminants. Even in such cases, the additive package can only handle so much contamination before these by-products begin depositing on engine parts. Sludge formation begins when the chemically suspended particles of contaminants, including the metal particles from engine wear, begin to settle out of the oil depositing anywhere the oil flows (Kaufman M., 2002).

Another cause of sludge is running the engine low on oil for a prolonged period of time. The detergent and oxidation inhibitors are important components of the additive package that prevent sludge from forming. When an engine is run low on oil, there are less additive available to protect the engine, suspending particles and

preventing oxidation (thickening) of the oil. Running an engine just 15-20% low for about 55 hours can increase the viscosity, or the thickness, of the oil by over 1000%. When engine oil gets this thick, it's a safe bet that the additive packet is shot and the oil is no longer actively suspending contaminants or neutralizing corrosives. This causes your oil to effectively damage your engine and not protecting it (Kaufman M., 2002).

Oil sludge from the internal combustion engine is the breakdown product of over-stressed oil. Oil that is stressed by contaminants and oxidation has to work thousands of miles longer than it was designed to and it will break down into a gel that sticks to the engine parts. As the sludge sticks, there is less good oil to circulate and do its protective job. This coating of gel also stores heat instead of releasing it which stresses the radiator and cooling system (Synthetic Performance Solutions, 2007-2008).

Every year, more of my customers suffer through unnecessary and very expensive engine re-builds due to oil sludge. The causes are complex but sludge damage can be prevented. The problem has been controlled by the type of oil used and also the invention of different engine designs (Norris S. and McCalmont M., 2005).

2.1 Advantages and Disadvantages of Recycling Spent Lubricant into Base Oil

2.1.1 Advantages

Cars, trucks, farm machines and boats all need regular lubricating oil changes. While some engines such as two-stroke engines burn oil completely, others like motor vehicle engines and machinery produce large volumes of used oil that can

be reclaimed and reused. Used oil should not be thrown away. Although it gets dirty, used oil can still be cleaned and re-used. In fact, recycled used oil can be used as an industrial burner fuel, hydraulic oil, incorporated into other products or re-refined back into new lubricating oil (El-Fadel and Khoury R. M., 2004).

Used oil is hazardous. Any spill or mismanagement in the disposal of the used lubricating oil can pose as a severe hazard to the environment and the surroundings. Lubricating oil picks up a variety of hazardous contaminants when used in engines and transmissions including lead, dioxins, benzene and polycyclic aromatics (Boughton and Horvath, 2003).

Mankind, the proud creator of wastes is anxiously watching today the harmful effects of its own creation on the environment and ultimately on its existence in this beautiful world. Scientists have developed different technologies like incineration with power production, pyrolysis, pelletization, dumping in landfill area, recycling of non-biodegradable wastes and composting of biodegradable wastes (Diaz L. F. and Golueke C. G., 1985). The first four are destructive approach while last two are constructive approach with value addition to wastes.

The challenge is to combine this with continuing economic growth in a way which is sustainable over the long term (Odum HT., 1996). The technologies of recycling have been developing in order to cope with increasing prices of oil. It is now more viable for the recycling process to take place as there is severe depletion in the natural resources of crude petroleum. It is because there are a lot of advantages that can be gained by recycling spent lubricant into base oil. The advantages are discussed below:

2.1.1.1 Slows the consumption of natural resources

We know that recycling involves the processing and usage of the core elements of an old product for the production of new products. This helps in saving

our natural resources to a great extent. Making a brand-new product without any recycled material causes natural resources to deplete in the manufacturing process. For example, less crude petroleum is used to produce lubricant if more and more used lubricant is recycled and reused. This way, proper recycling can help us preserve our natural resources for our future generations and maintain the balance of the nature (Chian *et al.*, 1976).

2.1.1.2 Recycling Saves Space for Waste Disposal

Most of the landfill sites are filled up with a lot of waste products that could have been recycled effectively. Some of these waste materials belong to non-biodegradable category which takes a long time to decompose. Recycling enables proper usage of these waste products and saves space for landfills. The pace with which landfills are getting filled up, soon we might run short of landfills unless we start following recycling at our own home and spread the word to others. One of the main reasons for recycling is to reduce the amount of garbage sent to landfills. Even though modern sanitary landfills are safer and less of a nuisance than the open dumps of the past, no one likes having a landfill around. In heavily populated areas, landfill space is scarce. Where space is plentiful, filling it with garbage isn't a very good solution to the problem (Diaz L. F. and Golueke C. G., 1985).

2.1.1.3 Recycling uses less energy

There is room for debate on this aspect of recycling, but many recycling processes require less energy than it would take to manufacture the same item brand-new. When new products are manufactured from the raw material obtained from recycled products, it saves a lot of energy which is consumed for the production. When new products are manufactured from ‘virgin materials’ the amount of energy consumed is much higher. Besides, the energy required to acquire and transport the ‘virgin’ raw materials from their origins or natural sources is also saved. Add to that

the energy which is required to clean and protect the environment from the pollutant waste products, especially those which are non-biodegradable (plastic) and fill up the landfill areas. Energy use is a factor weighed on a case-by-case basis (Odum HT., 1996).

2.1.1.4 Recycling saves environmental conditions and reduces pollution

Recycling helps in preventing global climate change to a great extent. By minimizing the energy spent on industrial production, recycling also helps in reducing greenhouse gas emission. All these emit harmful gases such as methane, sulfur dioxide, carbon dioxide to the environment. The processing of fresh raw material also creates toxic materials which pollute the environment. By reducing the energy used, recycling also minimizes the amount of fuel usage which in turn reduces the amount of harmful pollutants in the environment (Shie J. L. *et al.,* 2003).

Recycling also reduces pollution from landfill leachate. Landfills cause other problems in addition to taking up lots of space. The assortments of chemicals thrown into landfills causes leachate as a result of garbage break down. Used oil is a known source to cause leachate as dumping of used oils will create an easier way for the leachate to form. This is because the oil is in liquid form and blends with other toxic material which later seeps into the ground easily. Leachate can drain out of the landfill and contaminate groundwater supplies. Today, impermeable clay caps and plastic sheeting prevent much of this run off, making the landfills much safer than they were just a few decades ago. Still there are leachate that seep pass this barriers and pollute the environment (Albers H. and Mennerich A., 1986).

2.1.1.5 Economic Benefits

Similar to energy and natural resource, recycling also helps in saving a lot of expense, demanded for the production of new products from ‘virgin’ materials.

These expenses include the entire production cycle starting from acquiring the raw materials, transferring them from their origin to production places, processing and manufacturing costs (Bartone C. R., 1990).

Recycling process creates employment opportunities for a lot of people, involved in the various stages of the process. This in turn contributes to the economic development of the state or country.

Recycling has a variety of economic impacts. For the companies that buy used goods, recycle them and resell new products, recycling is the source of all their income. For cities in densely populated areas that have to pay by the ton for their landfill usage, recycling can shave millions of dollars off municipal budgets. The recycling industry can have an even broader impact. Economic analysis shows that recycling can generate three times more revenue per ton as landfill disposal and almost six times as many jobs (Diaz L. F. and Golueke C. G., 1985).

2.1.2 Disadvantages

The reprocessing of recovered materials is not always pollution free. Certain reprocessing technologies create residues which are difficult to treat. The acid-clay process for re-refining waste oil is one example where the residual sludge has contaminated land. Whether the use of recycled material is less polluting can only be assessed on a project by project basis (Boughton and Horvath. 2003).

The costs of collection transport and reprocessing may be a disadvantage. This also results in higher costs for recycled materials.

The emphasis upon packaging means that a great deal of effort goes into extending the recycling of materials which account for only one tenth of total urban waste by weight. It also means that the focus is upon products such as used lubricant which are conspicuous in litter. Even a small part of used lubricant in the waste

stream will have major adverse environmental effects. A drop of oil can spread on the surface of water in a big scale causing the lack of oxygen transfer in the water thus killing organisms in it. Some of these recycling schemes may bring no net gain to the community (Shie J. L. *et al.*, 2003).

2.1.2.1 No hassle free collection centre

A number of different systems have been implemented to collect recyclates from the general waste stream. These systems tend to lie along the spectrum of trade-off between public convenience and government ease and expense. The three main categories of collection are "drop-off centers", "buy-back centers" and "curbside collection" (Bartone C. R., 1990).

Drop-off centers require the waste producer to carry the recyclates to a central location, either an installed or mobile collection station or the reprocessing plant itself. They are the easiest type of collection to establish, but suffer from low and unpredictable throughput. Buy-back centers differ in that the cleaned recyclates are purchased, thus providing a clear incentive for use and creating a stable supply. The post-processed material can then be sold on, hopefully creating a profit. Curbside collection encompasses many subtly different systems, which differ mostly on where in the process the recyclates are sorted and cleaned. A waste collection vehicle generally picks up the waste (Bartone C. R., 1990).

There is still no specific way of collecting or distributing used oil in order to recycle it. This poses as a hassle to automobile repair shops as well as to other sources where the used lubricant can be obtained. Therefore the government should come up with a sound and collective ruling that states the way of disposal for used oils. The implementation of new rules will increase the awareness of people in the benefits of recycling thus increasing the recycling rate (Bartone C. R., 1990).

2.1.2.2 Mixed waste collection causes further problem

At one end of the spectrum is mixed waste collection, in which all recyclate are collected, mixed in with the rest of the waste, and the desired material is then sorted out and cleaned at a central sorting facility. This results in large amounts of recyclable waste being too soiled to reprocess. Public education is needed to change the mindset of people (Shie J. L. *et al.*, 2003).

Source separation is the other extreme, where each material is cleaned and sorted prior to collection. This method requires the least post-collection sorting and produces the purest recyclate, but incurs additional operating costs for collection of each separate material. This sort of processes requires a lot of cleaning process. Therefore it is more expensive and sometimes not feasible (Bartone C. R., 1990).

2.2 Machine and apparatus utilized

Many equipments and apparatus were utilized during the experiment. The machines used are discussed more below.

2.2.1 Centrifuge

Centrifugation is a process that involves the use of centrifugal force for the separation of mixtures, used in laboratory settings. More-dense components of the mixture migrate away from the axis of the centrifuge, while less-dense components of the mixture migrate towards the axis. Chemists may increase the effective gravitational force on a test tube so as to more rapidly and completely cause the precipitate to gather on the bottom of the tube. The remaining solution is called the supernatant liquid. The supernatant liquid is then either quickly decanted from the tube without disturbing the precipitate (Harrison *et al*., 2003).